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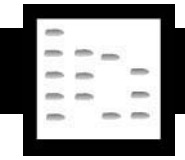
CRUDE OIL: LIQUID CHROMATOGRAPHY



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Introduction

Chromatographic methods that utilize liquid mobile phases include open-column liquid chromatography, high performance liquid chromatography (HPLC), size exclusion chromatography (SEC) and thin-layer chromatography (TLC). These techniques have been widely applied for the evaluation of crude oils (as well as their subfractions) for their quality, processability or hazards. This overview covers various approaches to the characterization of crude oils by these techniques. Specific applications, operational advantages and limitations of these methods are also highlighted.

The major applications of open-column liquid chromatography and HPLC to the characterization of crude oils and related materials including residua, topped crude oils, coal liquids or shale oils involve preparative fractionation for the determination of hydrocarbon types or class separation to be followed by the determination of important subgroups and individual components. There are also numerous reports where analytical HPLC with various detection schemes has been applied to the quantitative characterization of crude oils as well as other fossil fuels.

Crude oils are usually fractionated into several compound classes according to their molecular structures. A majority of class separations have dealt with the determination of saturates, aromatics, resins (or polars) and asphaltenes (SARA). Saturates consist of paraffinic and naphthenic compounds. If olefins are present in the sample, they are usually grouped with saturates. Aromatics range from alkylbenzenes (and other monoaromatics) to polycyclic aromatic hydrocarbons (PAHs). The polars are usually aromatic in nature and consist of compounds that may contain nitrogen, sulfur and oxygen as heteroatoms. Asphaltenes are highly condensed aromatic structures.

Conventional TLC with silica and alumina adsorbents provides separation of components from crude oils based on their polarity. TLC with flame ionization detection (TLC-FID) has been applied for the determination of hydrocarbon types. SEC has been particularly useful for the characterization of heavy crude oil fractions.

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Open-Column Liquid Chromatography

Crude oils have been fractionated into saturates, aromatics, resins and asphaltenes using open-column liquid chromatography. Asphaltenes are *n*-pentane, *n*-hexane- or *n*-heptane-insolubles depending on the *n*-alkane used. The *n*-alkane-soluble materials, termed maltenes, are usually fractionated on a silica or alumina column using appropriate solvents. In general, saturates are extracted with an *n*-alkane (such as *n*-hexane) followed by elution of aromatic and polar fractions with solvents or solvent mixtures of higher eluotropic strengths. Quantitative data are obtained by the gravimetric determination of each fraction after evaporation of solvent or solvent mixture. Rotary evaporation under mild vacuum is a common practice for the concentration of the collected fractions.

A crude oil separation scheme is shown in **Figure 1**. Maltenes are obtained by precipitation of asphaltenes from the crude oil using *n*-heptane. Using column liquid chromatography on alumina, and solvents or solvent mixtures as indicated in Figure 1, fractions enriched with saturates, aromatics I and II and polars can be obtained. The aromatics I fraction contains

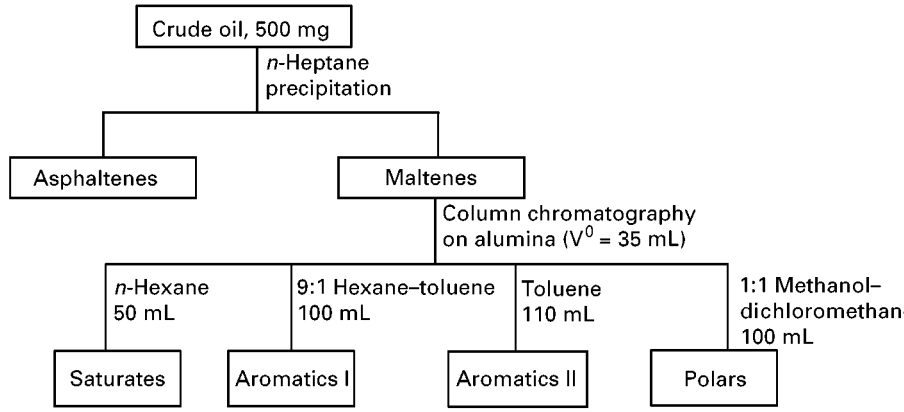

Figure 1 Fractionation of crude oil by open-column liquid chromatography. Column void volume $V^{\circ} = 35$ mL.

monoaromatics, and aromatics II fraction is composed of diaromatics and polycyclic aromatic compounds.

Many special separation schemes have been applied to obtain fractions enriched with specific types of compounds by tailoring the adsorbents as well as the eluting solvents. Beside enrichment and type separation of hydrocarbons, the following have been typical separation schemes for the characterization of crude oil.

1. Solubility fractionation of crude oil with solvents of increasing eluotropic strength, for example, in the order of *n*-pentane, cyclohexane, toluene and methylene chloride.
2. Crude oil fractionation of sulfur and nitrogen compounds for their characterization or identification by other methods.
3. Fractionation of PAHs for their determination, ring number distribution and degree of alkylation.
4. Fractionation of saturates into *n*-alkanes and cyclic plus iso-alkanes using a 0.5 nm molecular sieve column.
5. Fractionation of acidic and basic materials from crude oil using anion exchange and cation exchange resins, respectively.

ASTM D2007 clay-gel method (approved by the American Society for Testing and Materials for the determination of characteristic groups in rubber extender and processing oils and other petroleum-derived oils) has been applied to hydrocarbon-type determination of crude oils. In this method, two glass percolation columns are connected in series with the upper column containing clay and the lower one having clay at the top and silica gel at the bottom. The sample solution in pentane is added at the top of the upper column. *n*-Pentane is then used to elute saturates from clay and silica, leaving polars on the clay and aromatics on the silica. After removing residual aromatics from the clay adsorbent by washing with *n*-pentane, polars are desorbed with a 1 : 1 toluene–acetone mixture. Saturates and polars are determined gravimetrically by complete evaporation of solvents from the *n*-pentane and toluene–acetone fractions, respectively. The amount of aromatics is calculated by difference or, if desired, aromatics can be recovered by Soxhlet extraction using toluene.

Both small (mg or less) and large (multigram) scale fractionations of crude oil can be carried out by open-column solid–liquid chromatography to obtain fractions for further evaluation. These fractions are analysed by a host of analytical techniques such as gas chromatography (GC), pyrolysis GC, HPLC, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy. Elemental compositions for C, H, N, S, O, V and Ni can also be determined.

Class separation by open-column liquid chromatography is labour-intensive and often suffers from inaccuracies due primarily to overloading effects that result in cross-contamination of hydrocarbon types. Moreover, there is possible loss of light components during evaporation of solvent from a collected fraction that can add significant uncertainties in the quantitative data. There can also be recovery problems arising from irreversible adsorption of some compounds on the adsorbents.

High Performance Liquid Chromatography

Modern HPLC provides both preparative and analytical scale separation of hydrocarbon types from crude oils. Preparative separation is carried out primarily for gravimetric determination of hydrocarbon types after the removal of solvents from the collected fractions. HPLC offers flexibility to allow separation

of different compound types based on their polarity and affinity using various solvents and adsorbents. An HPLC system can also be automated. Since rapid fractionation of materials for collection is possible by HPLC, the method offers a much desired alternative to lengthy and multistep open-column liquid chromatography.

Crude oils are complex materials consisting of hundreds of individual compounds of different sizes and molecular structures. The resolution level obtained during initial separation of crude oil for compound classes by HPLC is often marginal. Therefore, when determination of individual compounds or functionalities is involved, fractions from the initial HPLC separation are subjected to offline or online analysis by high resolution chromatographic or spectroscopic techniques.

Columns and Solvents

Both analytical and preparative scale separations of hydrocarbon types by HPLC have been carried out on commercially available silica, aminopropylsiloxane-bonded silica, 2,4-dinitroanilinopropylsiloxane-bonded silica or cyanopropylsiloxane-bonded silica columns. Amino- and cyanopropylsiloxane columns have been used extensively in the class separation of crude oils and other fossil fuels.

n-Hexane and *n*-heptane have been the most commonly used mobile phases for the separation of saturates from other hydrocarbon classes. Mobile-phase modifiers such as methylene chloride, chloroform, tetrahydrofuran, methanol or 2-propanol have also been used to facilitate the elution of aromatics and polars.

Preparative columns can be much larger in size (with typical column dimensions 80×0.6 cm compared to 25×0.46 cm or less for the analytical column) to allow the separation of a few tenths of a gram or more of sample in each run. The particle size of the porous packing materials can also be much larger than that for the analytical column (50–100 versus 5–10 μm). Typical flow rates for preparative separations are 20 mL min^{-1} or higher, compared to 2 mL min^{-1} or less for analytical separations. Separation times in both cases can be 30 min or less.

Detectors

The choice of detectors for the quantitative determination of various compound classes has been a major concern in HPLC. Conventional diode-array UV detector and differential refractive index (RI) detector are commonly used with HPLC. A UV detector is not suitable for saturates as they do not have chromophores. The response from a UV detector at a specific wavelength varies with the number of aromatic rings, or with the isomeric compounds having the same number of aromatic rings. The very small difference in the RI of *n*-hexane (or *n*-heptane) and saturates is a serious limitation of an RI detector to be highly effective for the determination of saturates. The RI responses from aromatics and polar compounds are much lower compared to those from UV detection. The response factors of different hydrocarbon types, defined as peak area per unit concentration for both RI and UV detectors, show variations with many factors, including the crude oil, column type, column dimensions and mobile phase. Therefore, experimental response factors are often determined by preparative separation and collection of different hydrocarbon groups followed by analytical separation and detection of the collected fractions. For hydrocarbon-type analysis, each calibration is only valid for samples of the same source of crude oil.

Some special HPLC detectors, including FID, mass spectrometric detector (MSD) and evaporative light-scattering detector (ELSD) have been used in conjunction with HPLC separation of crude oils or their high boiling residua. These detectors have some attractive features. FID and ELSD are more sensitive than RI detectors and provide reasonably uniform response factors for different hydrocarbon types. MSD provides detection of materials with high sensitivity and specificity, and affords valuable information on molecular weight, structure and functionality of the molecules.

Although both FID and MSD have been successful as universal detectors in gas chromatography, the use of these detectors with HPLC has been limited, primarily because of the lack of effective interfaces to remove the mobile phase and to transport the sample to the detection system. A rotating disc FID has been demonstrated with samples boiling above 340°C to obtain hydrocarbon-type data covering a wide range of compositions. HPLC-MSD with thermospray or moving belt interface has been applied to the characterization of heavy hydrocarbons.

The ELSD has been applied to the hydrocarbon-type determination of fossil fuels boiling above 315°C (600°F). With the ELSD, mobile phase containing the analyte is nebulized with an inert gas (such as nitrogen) and sprayed into a heated drift tube where the mobile phase is vaporized, leaving behind a fine mist of dry micrometre-sized droplets in solvent vapour. As the sample particles pass through a flow cell, they scatter light from a laser beam to produce a signal. The mass versus signal from ELSD is usually nonlinear. However, the signal can be linearized using a power–law model $c = ms^b$, where c and s are mass

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and signal, and m and b refer to the proportionality constant and power–law exponent, respectively.

Element-specific detectors such as graphite furnace atomic absorption (GFAA) detector and inductively coupled plasma–atomic emission spectrometry (ICP-AES) detector have been interfaced with HPLC for the speciation of metal-containing compounds, including metal porphyrins. Electrochemical detectors have been applied to the detection of electroactive compounds such as phenols.

Separation Schemes

There have been a few efforts to optimize separation between hydrocarbon groups or subgroups. Most involve trials with the separation and detection of model compounds expected to be present in the sample. In almost all previous HPLC studies of crude oils and related materials, instruments have been automated for separation, detection and collection of fractions.

A simple HPLC separation scheme (scheme A) is shown in **Figure 2** where a single six-port valve and a single column (or a series of columns) have been used. Usually, deasphalted crude oil solution in hexane is injected for analysis by HPLC. The saturates and neutral aromatics (monoaromatics, diaromatics, triaromatics and tetraromatics) are separated first with the forward flow of hexane. After this, the valve-switching causes a reversal of mobile-phase flow through the column, allowing the backflushing of the column for the elution of polar compounds. The cut point between saturates and aromatics is determined by an RI detector while cut points between aromatic ring subfractions as well as polar compounds are determined by a UV detector.

Both resolution and selectivity of hydrocarbon type separations can be enhanced using different column types and multiple mobile phases during a single run. A solvent with higher eluotropic strength than an n-alkane or a multisolvent step gradient has been found to be more effective for total recovery of aromatic and polar compounds.

A separation scheme B (reported by Pearson and Gharfeh, 1986) utilizes two pumps, two six-port valves, one cyanopropyl silica column and two aminopropyl and cyanopropyl silica columns. Using n-hexane from the first pump, the sample is allowed to pass through the cyanopropyl silica column where polar compounds are strongly retained. The saturates and aromatics pass on to the two aminopropyl and cyanopropyl silica columns. The cyanopropyl silica column is then isolated using the first switching valve. As soon as the saturates elute, the second valve is used to backflush the aminopropyl and cyanopropyl silica columns for the elution of aromatics. The polar compounds are then eluted by back flushing the cyanopropyl silica column with methyl *tert*-butyl ether from the second pump. **Figure 3** shows a chromatogram of a crude oil residue obtained by the separation scheme B using FID for detection. Since a crude oil residue meets the boiling point requirements for an ELSD to be quantitative, ELSD can also be applied to detect and determine its components separated by HPLC.

Special HPLC Applications

Both preparative HPLC and analytical HPLC have been utilized for sample clean-up and separation of specific groups of compounds for online or offline characterization by capillary GC, GC-mass spectrometry (MS) or GC-element-specific detection. Column-liquid chromatography or semipreparative

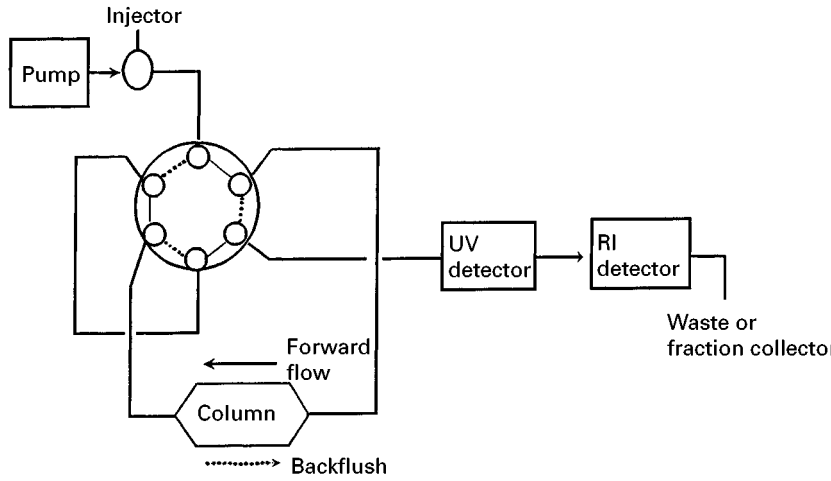

Figure 2 A scheme for hydrocarbon-type separation from crude oil by HPLC.

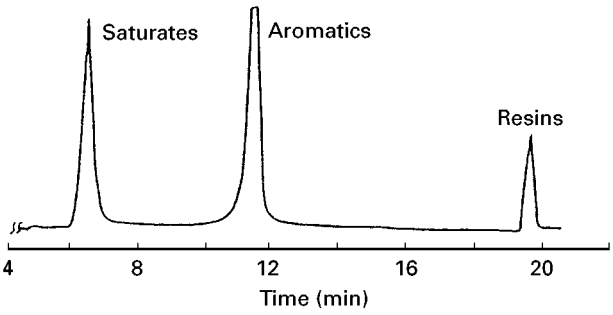

Figure 3 HPLC chromatogram of a crude oil residue. (Modified with permission from Pearson and Gharfeh, 1986. Copyright 1986 American Chemical Society.)

HPLC fractionation followed by analytical HPLC have also been very effective for the determination of certain compound types, including PAHs, petroporphyrins, sulfur heterocycles, phenols and nitrogen bases such as azarenes.

Size Exclusion Chromatography

SEC is usually applied to the analysis of high molecular weight materials. Unless there are specific interactions between the column packing and the sample components, the elution of molecules in SEC is bounded by limits representing total exclusion and total permeation through macroporous particles packed into a column. In this method, the high molecular weight materials elute first, followed by smaller molecules, which is the basis for the determination of molecular weight distribution by SEC.

Typical crude oils contain compounds having low (<100 Da) to high molecular weights (>2000 Da). The average molecular weight can be around 1000–1500 Da. Since 30% or more of the materials in the crude oil may have molecular weights similar to that of the mobile phase and therefore, falling close to the total permeation limit of typical SEC columns, SEC is more suitable for the determination of molecular weights of heavy petroleum fractions derived from crude oil. Atmospheric or vacuum residua and polars and asphaltene fractions from crude oil have been analysed by SEC to monitor changes during their processing or to fractionate them into narrower cuts for further analysis. SEC can also be used as a sample clean-up technique to remove small molecules from high molecular weight materials or vice versa.

The analysis of crude oil or its fractions by SEC is carried out using a series of small pore size (usually ≤ 100 nm) poly(styrene-divinylbenzene) columns and mobile phases of tetrahydrofuran, toluene, chloroform, *N*-methyl-2-pyrrolidone or pyridine. The sample size can be 5 mg or less. Almost all detectors used with HPLC can be coupled with SEC. The most common detectors are RI, ELSD and UV. Typical separation times are 40 min or less.

Usually molecular weight distributions of fossil samples are determined relative to narrow polystyrene standards. Although both RI and ELSD provide mass versus molecular weight distribution of the sample, a UV detector can be used for similar distribution for specific compound type, using a compound-specific wavelength. For example, distribution of petroporphyrins in polar fractions can be obtained by monitoring sample elution with a UV detector at around 400 nm. Petroporphyrin distributions have also been obtained by SEC-GFAA and SEC-ICP-AES detections.

Thin-Layer Chromatography

TLC using silica or alumina plates and appropriate solvents can provide quick class separation of a crude oil primarily for collection of its fractions. The detection methods for the separated components include visual examination of coloured spots, observation by irradiation with UV light, UV-fluorescence scanning and spraying of chromogenic or fluorogenic reagents.

Rapid and direct determination of hydrocarbon types of a crude oil can be achieved by TLC coupled with FID. In TLC-FID (which is also known as Iatroscan), thin reusable quartz rods (Chromarods) sintered with micrometre-sized silica or aluina particles are used as the stationary phase. After spotting a few micrograms of the sample, the Chromarods are developed sequentially with several solvents or their mixtures of decreasing eluotropic strengths to achieve desired separation. For example, the Chromarods can be developed first with toluene for 5 min to separate saturates plus aromatics from polar compounds. After this, they can again be developed with an *n*-alkane (such as *n*-heptane) for 30 min, for the separation of saturates from aromatics. During the second step, the position of polar compounds remains unchanged, and aromatics are distributed broadly according to their polarity or the number of aromatic rings. As an option, polar compounds can also be subdivided into two resin types by developing the Chromarods with a 9:1 chloroform–methanol mixture for 3.5 min. The Chromarods are dried in an oven after each development. Finally, each Chromarod is scanned by passing it through an oxygen–hydrogen flame for the detection of separated components.

Due to limitations in the design of the commercially available instruments, the TLC-FID method is only quantitative for samples boiling above 300°C. The low boiling materials present in the whole crude oil evaporate during development and drying. Such

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evaporation may also occur when Chromarods are exposed to the flame during scanning of the adjacent rod. Therefore, TLC-FID is more suitable for high boiling residua or fractions derived from crude oils than for whole crude oils.

The three TLC-FID chromatograms in **Figure 4** have been obtained by developing Chromarods with toluene for 5 min followed by *n*-heptane for 30 min. Figure 4A demonstrates the capability of TLC-FID for the resolution of saturates and aromatics, and of the ring-based separation of aromatic compounds. Peaks 1–5 in this chromatogram are for Nujol, *n*-heptadecylbenzene, 2,3-dimethylnaphthalene, 9-methylanthracene and 9,10-dimethyl-1,2-benzanthracene, respectively. The unidentified peaks (right-hand side of Figure 4A) are for polar impurities. A cursory examination of chromatograms of a topped crude oil in Figure 4B and of a vacuum residue in Figure 4C suggests a marked compositional difference between these two samples. Note that the vacuum residue was derived from the topped crude oil as vacuum tower bottoms after vacuum distillation. The vacuum residue contains much more polar and large ring aromatic compounds than the topped crude oil. Specifically, the amounts of saturates, aromatics and polars are 28.6, 56.8 and 14.6% (w/w) in the topped crude oil compared to 9.0, 58.5 and 32.5% (w/w), respectively, in the vacuum residue.

Unlike model aromatic compounds in Figure 4A, aromatics in both topped crude oils and vacuum residua do not show distinct peaks for different ring types. This is primarily due to chromatographic over-

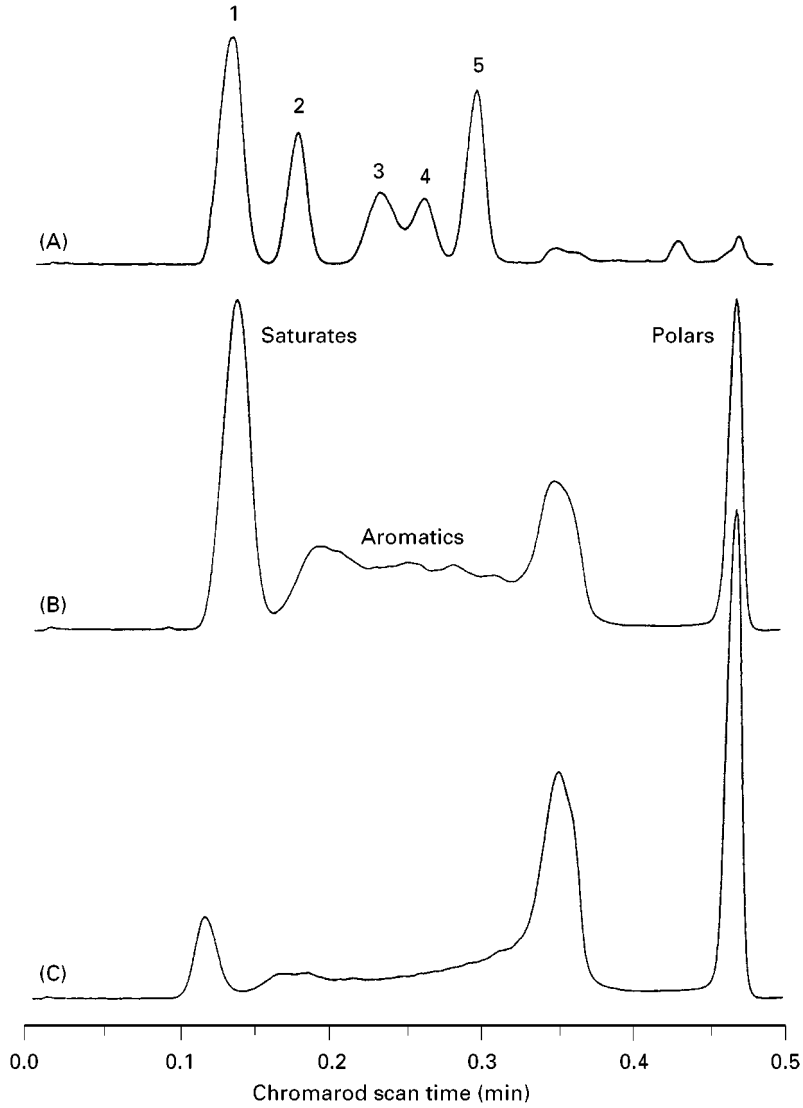

Figure 4 TLC-FID chromatograms. (A) Separation of hydrocarbons by class and number of aromatic rings using a model mixture described in the text; (B) topped crude oil; (C) vacuum residue.

lap arising from degree of substitution as well as substituents of diverse chemical structures attached to the monoaromatic as well as polycyclic aromatic compounds.

Future Possibilities

At present, relevant analytical data on crude oil composition are very useful in crude oil processing as petroleum refiners are increasingly using blended feeds instead of limiting the plant operation to a single type of crude oil. The compositional data will be more important as the depletion of light and sweet crude oils continues and refineries process more heavy and sour crude oils. For process control, product quality, catalyst performance and environmental compliance, faster and better analytical approaches to crude oil characterization will become a vital part of the refinery operation. As far as liquid chromatographic methods are concerned, multistep column-liquid chromatography will be less attractive due to limitations such as lengthy turnaround times, high level of uncertainties in the compositional data, excessive solvent consumption and costs involved in their disposal. Modern HPLC, SEC and TLC-FID methods will continue to provide valuable information on crude oils. Most likely, faster and better results will be achieved through major developments in system automation for coupling these techniques with other chromatographic and spectroscopic methods. Such hyphenated techniques are already being pursued to find better approaches to the characterization of fossil fuels, including crude oils.

See Colour Plate 71.

See also: **II/Chromatography: Liquid:** Detectors: Ultraviolet and Visible Detection; Mechanisms: Size Exclusion Chromatography. **III/Flame Ionization Detection: Thin-Layer (Planar) Chromatography. Flash Chromatography.**

Further Reading

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DECANTER CENTRIFUGES IN PHARMACEUTICAL APPLICATIONS

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Centrifugation continues to perform a vital role in pharmaceutical process operations. In the 1990s new enhancements to the technology attracted many new areas of application. Growing demands for higher yields and dryer cell cake, punctuated by the pursuit of lower cost solutions, continue to keep high performance centrifuges at centre stage in the quest for better separation procedures. In addition, tighter regulations and inspection procedures continue to act as catalysts for the development of fail-safe